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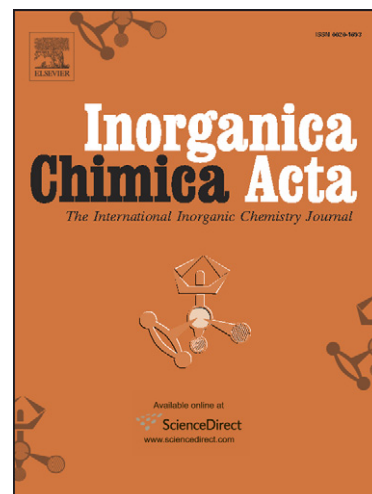
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Complexes of triphenylphosphine oxide with lanthanide bromidesAllen Bowden¹, Andrew W G Platt^{2*}, Kuldip Singh³ and Rachel Townsend²

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Abstract

The reaction between hydrated lanthanide bromides and triphenylphosphine oxide in 1:3 and 1:4 ratios in ethanol gave a series of complexes $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]\text{Br}$ (Ln = Pr, Nd, Gd, Tb, Er, Yb, Lu) which contain ethanol and water in the lattice, regardless of the ratio of reactants used. The single crystal x-ray structures of $[\text{NdBr}_2(\text{Ph}_3\text{PO})_4]\text{Br}$, $[\text{GdBr}_2(\text{Ph}_3\text{PO})_4]\text{Br}$ and $[\text{YbBr}_2(\text{Ph}_3\text{PO})_4]\text{Br}$ have been determined and have an octahedral geometry about the metal ion. Analysis of the bond distances shows that the Ln-O and Ln-Br distance change in accord with the lanthanide contraction, but the non bonded Ln...P distances and the Ln-O-P angles differ significantly for the Yb complex. Conductivity and variable temperature ^{31}P NMR measurements in dichloromethane indicate that the complexes dissolve as $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]^+$ for the lighter lanthanides with further ionisation becoming progressively more important for the heavier metals. In methanol more extensive dissociation is apparent. The electrospray mass spectra obtained from methanol solution show $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]^+$ is present in high abundance in the gas phase with other species formed due to ligand redistribution, ionisation and solvolysis.

Introduction

The coordination chemistry of triphenylphosphine oxide with various lanthanide salts has a long history [1,2] where complexes such as $\text{LnX}_3(\text{Ph}_3\text{PO})_n$ ($\text{X} = \text{Cl}^-$, NO_3^- and NCS^- , $n = 3,4$) were characterised. The *tetrakis* complexes could be formed for the lighter lanthanides whilst the *tris* complexes were favoured for the heavier metals.

More recently complexes with lanthanide nitrates with simple phosphine oxides such as $\text{Ce}(\text{NO}_3)_3(\text{Ph}_3\text{PO})_2$ (EtOH) [3], $\text{La}(\text{NO}_3)_3(\text{Ph}_3\text{PO})_4(\text{Me}_2\text{CO})$ and $[\text{Lu}(\text{NO}_3)_2(\text{Ph}_3\text{PO})_4]\text{NO}_3$ [4], $\text{La}(\text{NO}_3)_3(\text{Ph}_2\text{MePO})_3$, $\text{La}(\text{NO}_3)_4(\text{Ph}_2\text{MePO})_{4.x}\text{Me}_2\text{CO}$ and $[\text{Yb}(\text{NO}_3)_2(\text{Ph}_2\text{MePO})_4]\text{PF}_6$ [5] have been structurally characterised. Lanthanide triflate complexes, $[\text{Ln}(\text{OTf})_2(\text{Ph}_3\text{PO})_4]$ OTf have been characterised for Ln = La, Nd, Er and Lu [6] and Ce [7]. Complexes between lanthanide chlorides and triphenylphosphine oxide have also been reported with *trans* $[\text{LnCl}_2(\text{Ph}_3\text{PO})_4]^+$

isolated in the presence of hexafluorophosphate, and *mer* $[\text{LnCl}_3(\text{Ph}_3\text{PO})_3]$ being formed depending on reaction conditions [8]. The complex *trans* $[\text{YCl}_2(\text{Ph}_3\text{PO})_4]\text{Cl} \cdot 2.5\text{EtOH} \cdot \text{H}_2\text{O}$ [9] is formed from yttrium chloride and Ph_3PO . In the presence of excess Ph_3PO and chloride ion acceptors complexes of $[\text{LnCl}(\text{Ph}_3\text{PO})_5]^{2+}$ can be obtained [9, 10]. Corresponding complexes of lanthanide bromides and iodides are less well reported. The structures of $[\text{YBr}_2(\text{Ph}_3\text{PO})_4]\text{PF}_6$ [9] and $[\text{Ml}_2(\text{Ph}_3\text{PO})_4]^+$ where $\text{M} = \text{La}, \text{Ce}, \text{Nd}$ and U [7] are all *trans* octahedral. We have investigated the reactions of triphenylphosphine oxide with lanthanide bromides in 3:1 and 4:1 ratios to establish whether compounds analogous to the chloro complexes and the reported $[\text{YBr}_2(\text{Ph}_3\text{PO})_4]\text{PF}_6$ are formed and whether its structure is representative of the lanthanides. We also wished to investigate the structures to determine whether the lanthanide contraction imposes the gross structural changes observed in the complexes with lanthanide nitrates [4].

Results and discussion

Synthesis

On mixing hot ethanolic solutions of hydrated lanthanide bromides and triphenylphosphine oxide in 1:3 and 1:4 ratios, and cooling the resulting solutions slowly overnight, crystals suitable for single crystal x-ray analysis formed spontaneously for most of the lanthanides. Regardless of the ratio of reactants used the same type of complexes were obtained. This is in contrast to the behaviour of lanthanide chlorides with triphenylphosphine oxide where both 1:3 and 1:4 complexes can be isolated. The exclusive formation of the *tetrakis* complexes observed here may be due to solubility characteristics or steric effects of bromide compared to chloride. The earlier members of the series either gave crystals which rapidly softened on standing and eventually resolidified (La), or crystallised only with difficulty (Ce).

When immediately isolated the infrared spectrum of the crystals of the La complex is very similar to those of the complexes of the heavier lanthanides, but contains an additional strong band at 1047 cm^{-1} assigned as $\nu_{\text{C-O}}$ of lattice ethanol. On standing for five minutes in air the spectra show a shift of the OH stretch from 3366 cm^{-1} to 3250 cm^{-1} with a corresponding increase in its intensity. This change is accompanied by a decrease in the intensity of the band at 1047 cm^{-1} , indicating the displacement of ethanol by water. The PO stretch also changes, with the initially intense peak at 1135 cm^{-1} decreasing in intensity and developing a shoulder at 1148 cm^{-1} . Elemental analysis of the La and Ce complexes did not conform to any formula analogous to those found for the remainder of the series. The analyses gave reasonable fits to $\text{La}_2\text{Br}_6(\text{Ph}_3\text{PO})_7(\text{H}_2\text{O})_7(\text{EtOH})_2$ and $\text{CeBr}_3(\text{Ph}_3\text{PO})_4(\text{H}_2\text{O})_3(\text{EtOH})$. Crystals suitable for x-ray diffraction studies could not be obtained for either the La or Ce complexes. The crystals obtained for the other lanthanides also rapidly lost solvent on standing in ambient conditions, but remained crystalline throughout the process. These complexes had to be stored in their mother liquor prior to crystallography. The loss of solvent is probably responsible for the variable elemental analysis obtained for the complexes and it was not possible to obtain consistent values across the range of complexes studied. The presence of water and ethanol in the crystals of analogous $\text{LnCl}_3(\text{Ph}_3\text{PO})_n$ complexes has been reported [8]. The infrared spectra of these complexes are as expected, being essentially that of a coordinated triphenylphosphine oxide with ν_{PO} shifted to lower wavenumber by about 40 cm^{-1} compared to the free ligand, giving an intense absorption at around 1140 cm^{-1} for all complexes. This lack of variation in ν_{PO} has also been reported in complexes such as $\text{LnX}_3(\text{Ph}_3\text{PO})_n$ ($\text{X} = \text{NCS}, \text{Cl}, n = 3,4$) [2]. There is clear evidence in the spectra of all complexes for the presence of lattice ethanol with weak C-H stretches at around 2966 cm^{-1} in addition to

the aromatic C-H stretch above 3000 cm^{-1} , and two absorptions at $\sim 1086(\text{s})$ and $1045(\text{m})\text{ cm}^{-1}$ assigned to ethanol by comparison with a standard spectrum. In addition a weak, broad O-H stretch is present at $3300 - 3330\text{ cm}^{-1}$ due to ethanol and water.

X-ray Structures

The single crystal x-ray structures of $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]\text{Br}$ ($\text{Ln} = \text{Nd}, \text{Gd}, \text{Yb}$) have been determined. These metals were chosen as representative of the range of lanthanides and any structural changes across the series would be evident in this study. Details of the data collection and refinement for the crystal structures are given in Table 1 and selected bond lengths and angles in Table 2. The decrease in R factors from Nd to Yb reflects the quality of the crystals obtained. The complexes have identical molecular connectivity and the structure of the Gd complex is shown in Figure 1 as a representative example. The complexes all have a slightly distorted *trans* octahedral arrangement of oxygen and bromine around the metal ion. The average of the *cis* bond angles is 90° for all the complexes with values of $90.0 \pm 2.8^\circ$ (Nd), $90.0 \pm 2.4^\circ$ (Gd) and $90.0 \pm 2.7^\circ$ (Yb). The *trans* angles depart slightly more from the octahedral norm with averages of $175.3 \pm 2.0^\circ$ (Nd), $175.8 \pm 1.8^\circ$ (Gd) and $175.6 \pm 3.0^\circ$ (Yb). The lanthanide ions and the four oxygen atoms of the phosphine oxides are essentially coplanar with the oxygen atoms lying within 0.1 \AA of the mean LnO_4 plane.

The bond distances to the lanthanide ions in the complexes show the expected decrease associated with the lanthanide contraction. Whilst such decreases are generally assigned to the lanthanide contraction, we have recently found that statistical analysis can reveal where other factors influence the observed bond distances [13]. The data for the compounds characterised here, and the analogous

yttrium complex [9], have been statistically analysed with the intention of identifying whether the lanthanide contraction alone is responsible for the observed decreases in Ln-O and Ln-Br distances. If the observed changes can be accounted for satisfactorily by decreases in the ionic radii of the metal, there should be no significant differences between [$d_{\text{Ln-O}} - 6$ coordinate ionic radius] and [$d_{\text{Ln-Br}} - 6$ coordinate ionic radius] for different lanthanides. This was assessed by carrying out a single factor ANOVA test over all data, and also including data from the $[\text{YBr}_2(\text{Ph}_3\text{PO})_4]^+$ cation [9], at a 95% confidence level. The result showed no significant differences and thus we can be confident that in this series of complexes, changes in distances to the metal ions across the lanthanide series can be explained by the lanthanide contraction alone.

The P-O-Ln angles approach the 180° expected on the basis of electrostatic repulsions between the positively charged phosphorus and lanthanide ion. The average values for the Nd and Gd complexes are essentially identical at $171.7 \pm 2.9^\circ$ and $171.5 \pm 3.2^\circ$ respectively. The values for the Yb complex at $161.0 \pm 4.8^\circ$ and the Y complex $164.1 \pm 7.1^\circ$ [9] appear significantly smaller. These differences should also be reflected in the non bonded Ln...P distances, which decrease along the series of complexes studied with averages of $3.81 \pm 0.02 \text{ \AA}$ (Nd), $3.76 \pm 0.01 \text{ \AA}$ (Gd), $3.69 \pm 0.02 \text{ \AA}$ (Y[9]) and $3.64 \pm 0.02 \text{ \AA}$ (Yb). Further analysis of the Ln...P distances corrected for the size of the lanthanide ion, as described above for the Ln-O distances, reveals that significant differences exist between the lighter Nd and Gd complexes and the Yb complex, which are shorter (the values of [$d_{\text{Ln...P}} - 6$ coordinate ionic radius] are $2.69 \pm 0.01 \text{ \AA}$ (Nd), $2.68 \pm 0.01 \text{ \AA}$ (Gd), $2.65 \pm 0.02 \text{ \AA}$ (Y) and $2.63 \pm 0.02 \text{ \AA}$ (Yb)).

The statistical significance of both the differences in the P-O-Ln angle and Ln...P distances were evaluated over the data for all four complexes. Significant differences

were found, at a confidence level of 95% by single factor ANOVA followed by post hoc t-tests, between the Yb complexes and the both Nd and Gd complexes. Whilst the difference in angles between the Y complex and the lighter lanthanides appears, at first sight to be large, there is no significant difference between the means due to the wider spread of angles found in this complex. This difference between the structure of the Yb complex and those of Nd and Gd can also be seen in the distance of the P-atoms from the mean LnO₄ plane. For instance the average distance for the Gd complex is $0.34 \pm 0.13 \text{ \AA}$ compared with $0.60 \pm 0.10 \text{ \AA}$ for the Yb complex. This is illustrated in Figure 2 where the structures of the Gd and Yb complexes are compared. Thus both the analysis of the Ln-O-P angles and the Ln...P distances indicate that as the size of the lanthanide ion decreases the increased non bonded repulsions in the peripheral structure are reduced by a bending of the Ln-O-P angle further away from linearity. This in turn brings about an increase in the electrostatic repulsions between the positive lanthanide and phosphorus centres. Thus the overall structure adopted will be governed by a subtle balance between increasing electrostatic repulsions and relief of steric strain.

Conductivity measurements

The conductivity of 0.001M solutions was determined to deduce whether the solid state structures are retained in solution. If the solids dissolve as $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]^+\text{Br}^-$ conductivity values consistent with 1:1 electrolytes should be obtained. The molar conductivities of 0.001 M solutions in methanol and dichloromethane at 20°C are shown in Table 3. In methanol a weak trend of increasing values from 0.0140 $\text{Sm}^2\text{mol}^{-1}$ for $[\text{CeBr}_2(\text{Ph}_3\text{PO})_4]^+\text{Br}^-$ to 0.0164 $\text{Sm}^2\text{mol}^{-1}$ for $[\text{LuBr}_2(\text{Ph}_3\text{PO})_4]^+\text{Br}^-$ is seen. These values are at the lower end of the range of 0.0160 – 0.0220 $\text{Sm}^2\text{mol}^{-1}$

generally associated with 2:1 electrolytes in methanol [10]. It must be noted however, that values for 0.001M solutions of CsCl and Et₄NCl in methanol of 0.0154 and 0.0150 Sm⁻²mol⁻¹ respectively, must be associated with 1:1 electrolytes[12], and that molar conductivity values 0.0127 and 0.0143 Sm⁻²mol⁻¹ have been interpreted in the same study as indicative of 1:1 electrolytes in methanol solutions of PrCl₃.6H₂O and PrCl₃. Thus the results here are ambiguous, and could be interpreted as either being indicative of a 1:1 electrolyte or of further partial dissociation perhaps due to the formation of species such as [LnBr(Ph₃PO₄)(MeOH)]²⁺.2Br⁻ in solution. A conductivity study of the analogous LnCl₃(Ph₃PO)₄ and LnCl₃(Ph₃PO)₃ complexes found that they were non conducting in acetone and probably 7 and 6 coordinate respectively [2], whilst a later study found that neutral molecular species were preferred by the early lanthanides with the ionic *tetrakis* complexes favoured by the heavier metals [8].

Although dichloromethane is not ideal for use in conductivity measurements due to the narrow range of conductivity values in this solvent [11] its use for such measurements has been reported. It is often a good solvent, even for ionic complexes, and it is unlikely to coordinate directly to the metal and thus will not induce further ionisation. Typical values seem to be in the region of 0.002 – 0.003 Sm²mol⁻¹ for 1:1 electrolytes [5,9] and a value of 0.0042 Sm²mol⁻¹ has been reported for the 2:1 electrolyte [YCl(Ph₃PO)₅]²⁺2[SbCl₆]⁻ [9]. The conductivities of [LnBr₂(Ph₃PO)₄]Br in CH₂Cl₂ increase from the accepted values for 1:1 electrolytes of around 0.002 – 0.003 Sm²mol⁻¹ (Ce, Pr, Nd) to values more consistent with 2:1 electrolytes in the region of 0.005 Sm²mol⁻¹ (Gd – Lu). It is possible that for the smaller lanthanide ions further ionisation of bromide ions giving more highly conducting species is occurring. Species such as [LnBr(Ph₃PO)₄]²⁺2Br⁻ would not be expected to be present to any

significant extent on the basis of the rather low coordination number. The formation of bromide bridged dimers such as $[(\text{Ph}_3\text{PO})_4\text{Ln}\mu(\text{Br})_2\text{Ln}(\text{Ph}_3\text{PO})_4]^{4+}4\text{Br}^-$, however, does maintain the coordination number to an acceptable level.

^{31}P NMR Spectroscopy

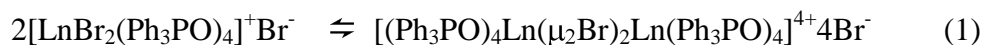
The ^{31}P NMR spectra of selected complexes have been studied at various temperatures in CD_2Cl_2 and CD_3OD .

The results are summarised in Table 4. At -90°C all the complexes show, in addition to signals from metal bound ligand, an additional low intensity signal at 29.4 ppm indicating that dissociation of Ph_3PO is occurring to a small extent. The assignment as Ph_3PO was confirmed by the addition of a small amount of the free ligand which caused an increase in the intensity of this resonance. A small broadening of the signals of the bound ligand in the spectra at room temperature was observed, but the presence of discrete resonances at very similar shifts, compared to those observed in the absence of additional Ph_3PO , indicated that there is no rapid exchange between free and bound ligand in CD_2Cl_2 .

The spectra for the Pr complex show a single peak which in conjunction with the conductivity data in CH_2Cl_2 suggest that the major species in solution is

$[\text{PrBr}_2(\text{Ph}_3\text{PO})_4]^+\text{Br}^-$. The spectra for the Tb, Er and Lu complexes all show two signals at room temperature and in view of the higher conductivity values in CH_2Cl_2 it seems reasonable to suppose that ionisation of a second bromide ion is occurring, rather than formation of neutral complexes such as $\text{LnBr}_3(\text{Ph}_3\text{PO})_3$. This further dissociation of bromide would lead to species such as $[\text{LnBr}(\text{Ph}_3\text{PO})_4]^{2+}2\text{Br}^-$ in solution in which the coordination number of the lanthanide ion would be lower than normally expected. It is possible that the formation of bromide bridged dimers,

suggested above, could maintain a higher coordination number around the metal and thus an equilibrium of the type shown in (1) could account for the higher



conductivities and the presence of two lanthanide containing species in solution.

There is no evidence for the presence of inequivalent P- atoms in the spectra of the Lu complex in CD_2Cl_2 at -90°C , and if such dimers exist in solution they must be fluxional on the NMR time scale.

The chemical shifts of all the paramagnetic species are strongly temperature dependent as shown in Figure 3. The temperature dependence of chemical shifts in paramagnetic complexes is well documented [14], and a similar effect has recently been reported for Nd and Ce complexes of 2,4-bis(diphenylphosphorylmethyl)mesitylene [15]. The temperature dependence of the chemical shift is linear for the Pr and Er complexes ($R^2 = 0.98$ in both cases) but gives a better quadratic fit for Tb ($R^2 = 0.99$ compared with 0.88 for a linear fit). In CD_3OD the ^{31}P NMR spectra are quite different showing intense broad peaks in the region of Ph_3PO for all complexes. The position of these signals does not change significantly on reducing the temperature and it appears that these complexes are extensively dissociated in methanol solution.

A freshly prepared solution of the Lu complex gave two broad signals at 34.4 (75%) and 40.2 ppm (25%); the latter assigned as $[\text{LuBr}_2(\text{Ph}_3\text{PO})_4]^+$. The line widths of the signals indicates that significant exchange between free and bound Ph_3PO occurs.

The proportion of these peaks does not change significantly on standing for one day indicating that the dissociation is less extensive than for the other lanthanide ions, presumably as a result of stronger electrostatic attraction between the smaller Lu^{3+} ion and Ph_3PO .

In conjunction with the high conductance values it seems probable that the complexes do not retain their original structures in solution with extensive dissociation / ionisation occurring in methanol.

Electrospray mass spectrometry

High resolution electrospray mass spectra were obtained for representative samples from methanol solution. The results with principle assignments are summarised in Table 5. Assignments are based on the comparison of the observed and calculated m/z values and the characteristic isotope patterns observed. The agreement between calculated and observed m/z values was better than 10ppm and an example of the comparison between the expected and observed m/z values and the isotope distribution pattern is shown for $[\text{TbBr}_2(\text{Ph}_3\text{PO})_4]^+$ in Figure 4 .

In all cases the $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]^+$ ion found in the solid state is observed in the gas phase, generally as the most abundant lanthanide containing ion. It thus appears that there is a smooth transfer of the expected ions in solution into the gas phase. The formation of ions during droplet evaporation leads to a relatively complex set of spectra with redistribution of the ligand and further loss of bromide ion to give species such as $[\text{LnBrL}_n]^{2+}$ ($n = 5, 4, 3$) and $[\text{LnL}_n]^{3+}$ ($n = 6, 5, 4$), and peaks assigned to $[\text{L}+\text{H}]^+$, $[2\text{L}+\text{H}]^+$, $[3\text{L}+\text{Na}]^+$ and $[4\text{L}+\text{Na}]^+$ present in the spectra of all the complexes.

In addition solvolysis reactions are apparent in the formation of ions such as



The negative ion spectra are much simpler showing peaks at $m/z = 79$ and 81 and at $m/z = 181, 183$ and 185 due to Br^- and $[\text{Br}^- + \text{NaBr}]$ respectively.

Conclusion

The lanthanide bromides on reaction with triphenylphosphine oxide form *tetrakis* complexes $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]\text{Br}$ as the only products for $\text{Ln} = \text{Pr-Lu}$. Complexes with La and Ce have been isolated but their exact nature is still uncertain. NMR and conductivity measurement indicate that solutions in dichloromethane contain an equilibrium between $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]^+$ and more highly charged species. In methanol extensive dissociation of Ph_3PO and Br^- is evident.

Experimental

X-ray crystallography

Data were collected on a Bruker APEX 2000 CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Details of data collection, refinement and crystal data are listed in Table 1.

The data were corrected for Lorentz and polarization effects and empirical corrections applied. The structures were solved by direct methods. The structure refinement on F² employed SHELXTL VERSION 6.10 [16]. Hydrogen atoms were included in calculated positions ($\text{C-H} = 0.95 \text{ \AA}$) riding on the bonded atom with isotropic displacement parameters set to 1.2 Ueq(C) for all H atoms. All non-H atoms were refined with anisotropic displacement parameters.

Disordered solvent was omitted using the SQUEEZE option in Platon [17] for all structures.

Mass spectra were obtained on a Thermofisher LTQ Orbitrap XL at the EPSRC National Mass Spectrometry Service Centre at Swansea University.

Infrared spectra were recorded with a resolution of $\pm 2 \text{ cm}^{-1}$ on a Thermo Nicolet Avatar 370 FT-IR spectrometer operating in ATR mode. Samples were compressed onto the optical window and spectra recorded without further sample pre-treatment.

^{31}P NMR spectra were recorded on a JEOL EX 400 at 161.8 MHz.

Conductivity measurements were made on 0.001 M solution of the complexes in methanol using a Hanna HI 9033 multi range conductivity meter.

The complexes were prepared by the same general method. Solutions of the hydrated lanthanide bromides (~1 mmol) in 5 ml hot ethanol and triphenylphosphine oxide (~ 4 mmol) in 5ml hot ethanol were mixed. Crystals were deposited on standing overnight. Samples for crystallography were removed, stored in the mother liquor and removed immediately before analysis. The bulk material was filtered, washed with a little cold ethanol and dried at the pump.

Details for individual compounds are summarised below.

Reaction of LaBr_3 with Ph_3PO : $\text{LaBr}_3 \cdot 7\text{H}_2\text{O}$ (0.43 g 0.85 mmol) and Ph_3PO 1.02 g 3.66 mmol) in hot ethanol when treated as above gave colourless crystals which rapidly softened in air eventually becoming crystalline on standing to give 0.68 g (53%).

Analysis: calculated for $\text{La}_2\text{Br}_6(\text{Ph}_3\text{PO})_7(\text{H}_2\text{O})_7(\text{EtOH})_2$ (found) C53.41(53.43) H4.52 (4.57); IR (ATR) $/\text{cm}^{-1}$ 3275 (m) (OH), 1150 (s), 1148(s) (PO), 1135(s) (PO), 1081 (s) (C-O);

Reaction of CeBr_3 with Ph_3PO : $\text{CeBr}_3 \cdot 7\text{H}_2\text{O}$ (0.53 g 1.05 mmol) and Ph_3PO 1.14 g 3.85 mmol) in hot ethanol when treated as above gave colourless crystals, 0.58 g (40%).

Analysis: calculated for $\text{CeBr}_3(\text{Ph}_3\text{PO})_4(\text{H}_2\text{O})_3$ (found) C55.90 (55.96) H4.30(4.00); IR (ATR) $/\text{cm}^{-1}$ 3271 (m) (OH), 1135 (s) (PO), 1080 (s) (C-O).

PrBr₃(Ph₃PO)₄.EtOH: PrBr₃6H₂O (0.55 g, 1.13 mmol) and Ph₃PO (1.08 g, 3.88 mmol) in hot ethanol when treated as above gave 0.65 g (38%) green crystals.

Analysis: calculated (found) C57.72 (57.48) H4.32 (4.26); IR (ATR) /cm⁻¹ 3306 (w) (OH),1140 (s) (PO),1086 (s) (C-O).

NdBr₃(Ph₃PO)₄.EtOH: NdBr₃6H₂O (0.53 g 1.08 mmol) and Ph₃PO (1.12 g 4.03 mmol) in hot ethanol when treated as above gave 0.86 g (50%) lilac crystals.

Analysis: calculated (found) C57.60 (57.48) H4.31 (4.22) IR (ATR) /cm⁻¹ 3306 (w) (OH),1141 (s) (PO),1086 (s) (C-O).

GdBr₃(Ph₃PO)₄.EtOH.3H₂O: GdBr₃6H₂O (0.52 g 1.03 mmol) and Ph₃PO (1.11 g 3.99 mmol) in hot ethanol when treated as above gave 0.96 g (58%) colourless crystals.

Analysis: calculated (found) C55.20 (55.15) H4.51 (4.22) IR (ATR) /cm⁻¹ 3306 (w) (OH),1141 (s) (PO),1086 (s) (C-O).

TbBr₃(Ph₃PO)₄.EtOH.3H₂O: TbBr₃6H₂O (0.53 g 1.05 mmol) and Ph₃PO (1.13 g 4.06 mmol) in hot ethanol when treated as above gave 0.92 g (55%) colourless crystals.

Analysis: calculated (found) C55.14 (54.59) H4.50 (3.66) IR (ATR) /cm⁻¹ 3306 (w) (OH),1140 (s) (PO),1086 (s) (C-O)

ErBr₃(Ph₃PO)₄.EtOH.H₂O: ErBr₃6H₂O (0.55 g 1.07 mmol) and Ph₃PO (1.16 g 4.17 mmol) in hot ethanol when treated as above gave 0.71 g (42%) pale pink crystals.

Analysis: calculated (found) C56.10 (56.17) H4.33 (3.94) IR (ATR) /cm⁻¹ 3324 (w) (OH),1141 (s) (PO),1086 (s) (C-O).

$\text{YbBr}_3(\text{Ph}_3\text{PO})_4 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$: $\text{YbBr}_3 \cdot 6\text{H}_2\text{O}$ (0.54 g 1.04 mmol) and Ph_3PO (1.14 g 4.10 mmol) in hot ethanol when treated as above gave 1.08 g (66%) colourless crystals.

Analysis: calculated (found) C 55.90 (55.73) H 4.31 (3.71) IR (ATR) $/\text{cm}^{-1}$ 3334 (w) (OH), 1140 (s) (PO), 1086 (s) (C-O).

$\text{LuBr}_3(\text{Ph}_3\text{PO})_4 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$: $\text{LuBr}_3 \cdot 6\text{H}_2\text{O}$ (0.56 g 1.07 mmol) and Ph_3PO (1.11 g 3.99 mmol) in hot ethanol when treated as above gave 0.90 g (53%) colourless crystals.

Analysis: calculated (found) C 55.83 (54.12) H 4.31 (3.66) IR (ATR) $/\text{cm}^{-1}$ 3306 (m) (OH), 1141 (s) (PO), 1086 (s) (C-O).

Attempted preparation of $\text{LnBr}_3(\text{Ph}_3\text{PO})_3$. The preparations were carried out in the same manner as described above for the 1:4 complexes. Solutions of the hydrated lanthanide bromides (~1 mmol) in 5 ml hot ethanol and triphenylphosphine oxide (~3 mmol) in 5 ml hot ethanol were mixed. Crystals were deposited on standing overnight and these were filtered washed with a little ethanol and dried at the pump. The infrared spectra were essentially identical to those described above.

$\text{PrBr}_3 \cdot 6\text{H}_2\text{O}$ (0.49 g 1.00 mmol) and Ph_3PO (0.90 g 3.04 mmol) in hot ethanol when treated as above gave 0.89 g (73% based on Ph_3PO) green crystals.

Analysis: calculated for $\text{PrBr}_3(\text{Ph}_3\text{PO})_4 \cdot \text{EtOH} \cdot (\text{H}_2\text{O})_2$ (found) C 56.40 (56.19) H 4.48 (3.83)

$\text{ErBr}_3 \cdot 6\text{H}_2\text{O}$ (0.50 g 0.97 mmol) and Ph_3PO (0.84 g 2.84 mmol) in hot ethanol when treated as above gave 0.93 g (81% based on Ph_3PO) green crystals.

Analysis: calculated for $\text{ErBr}_3(\text{Ph}_3\text{PO})_4 \cdot \text{EtOH} \cdot (\text{H}_2\text{O})_2$ (found) C 55.47 (54.94) H 4.40 (3.95)

YbBr₃·6H₂O (0.48 g 0.92 mmol) and Ph₃PO (0.84 g 2.83 mmol) in hot ethanol when treated as above gave 0.92 g (80% based on Ph₃PO) green crystals.

Analysis: calculated for PrBr₃(Ph₃PO)₄EtOH(H₂O)₂ (found) C 55.27 (54.72) H 4.48 (4.00)

Supplementary data

CCDC 733446, 733447 and 73448 contains the supplementary crystallographic data for the Gd, Nd and Yb structures respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK: fax (+44+ 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk

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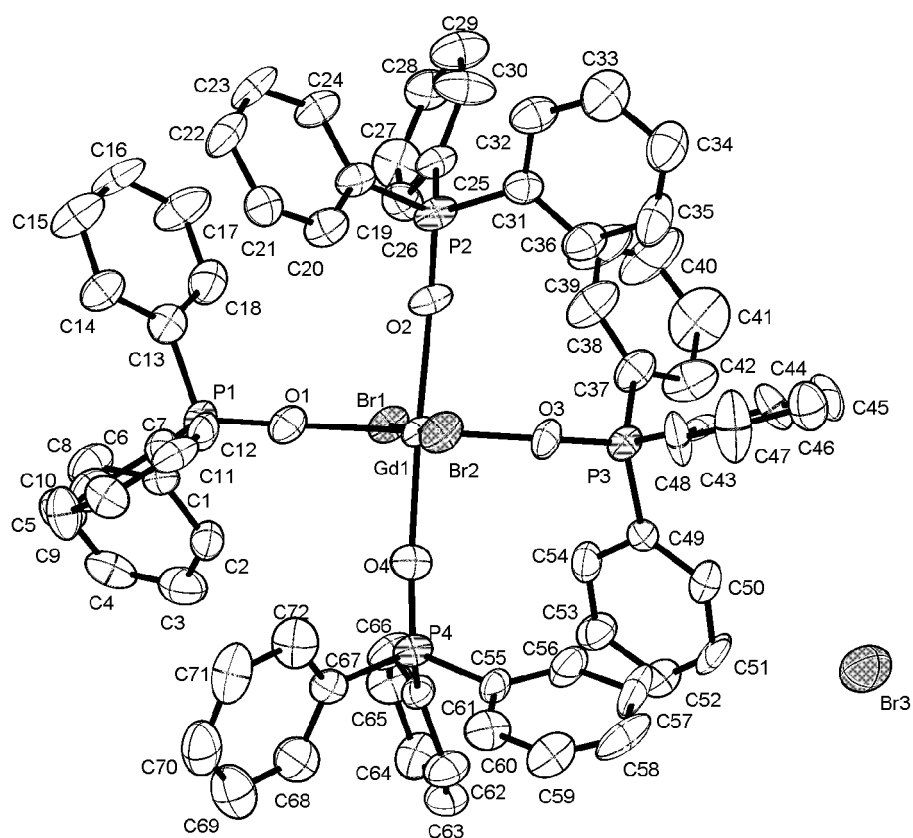


Figure1 The structure of [GdBr₂(Ph₃PO)₄]⁺[Br]⁻ showing 50% displacement ellipsoids. The hydrogen atoms have been omitted from the diagrams for clarity.

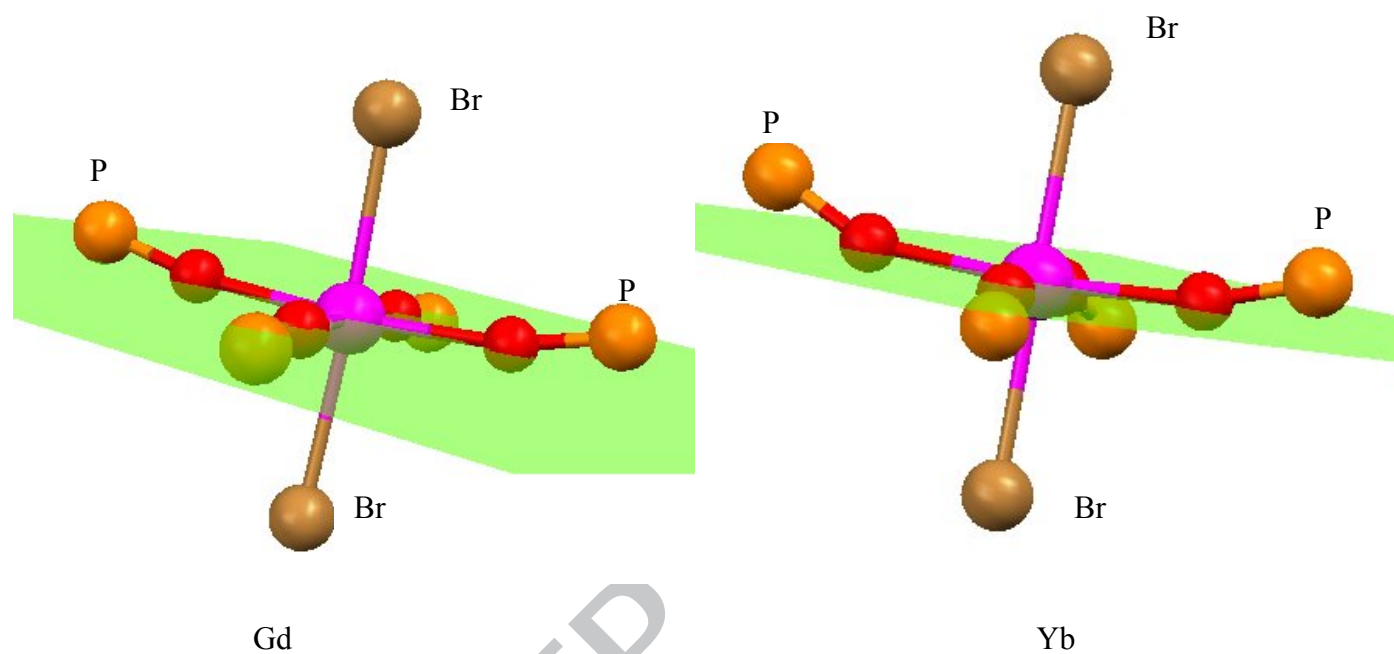


Figure 2 The core geometry of $[\text{GdBr}_2(\text{Ph}_3\text{PO})_4]^+$ and $[\text{YbBr}_2(\text{Ph}_3\text{PO})_4]^+$ showing the increasing deviation of the P atom from the mean LnO_4 plane

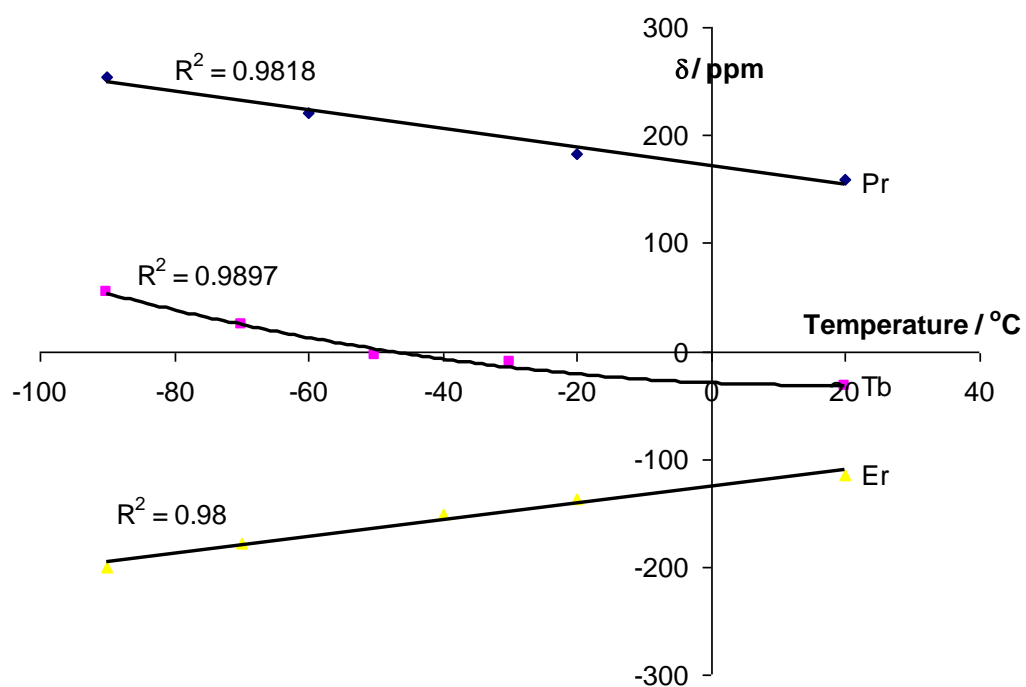


Figure 3 The variation in chemical shift with temperature for $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]\text{Br}$ ($\text{Ln} = \text{Pr, Tb, Er}$)

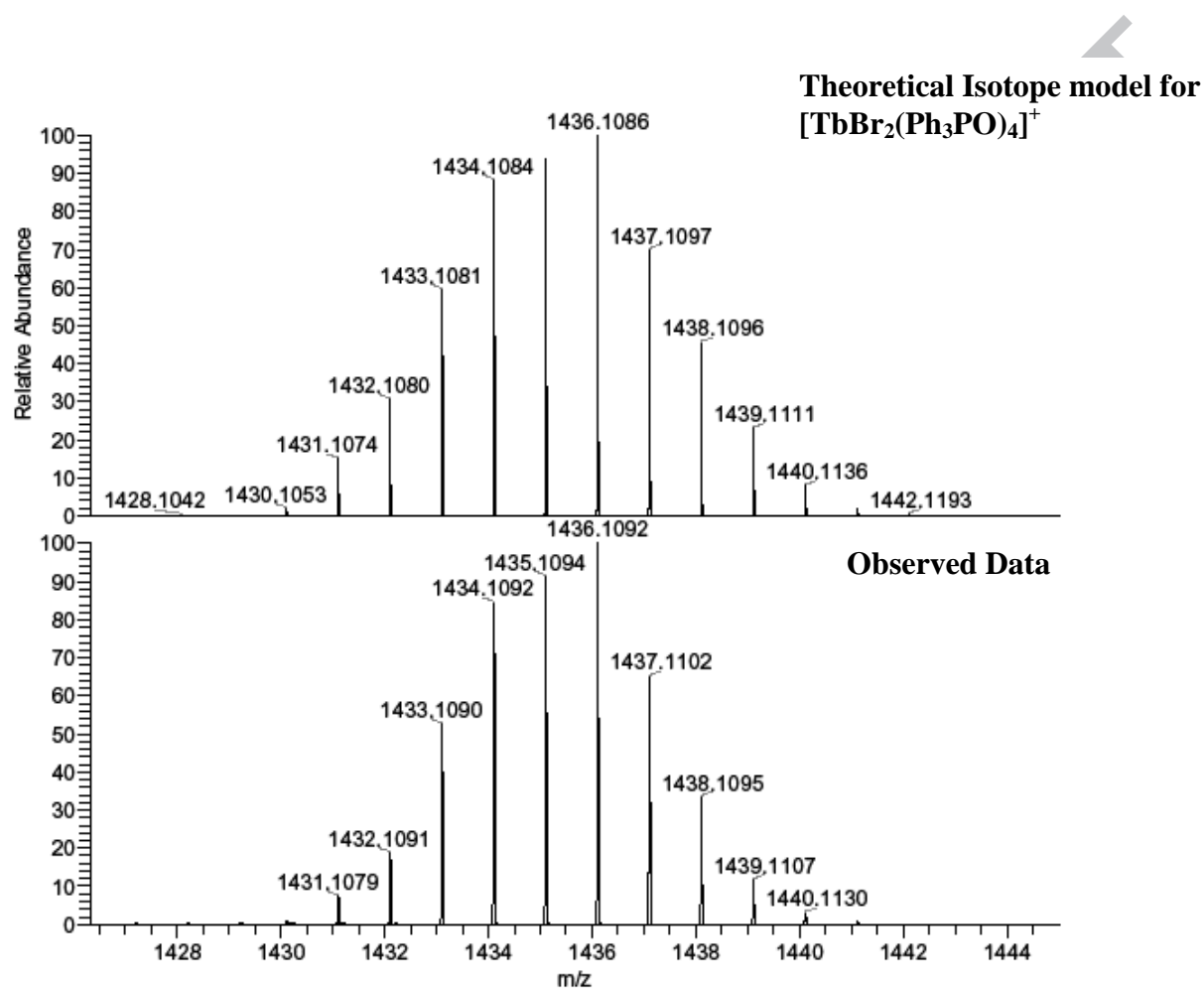


Figure 4 Theoretical and observed isotope patterns for the $[\text{TbBr}_2(\text{Ph}_3\text{PO})_4]^+$ ion

Table 1 Crystal data and structure refinement for the Nd, Gd and Yb complexes

Identification code	nd1	
Empirical formula	C ₈₈ H ₁₀₈ Br ₃ Nd O ₁₂ P ₄	
Formula weight		1865.59
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.356(3) Å b = 17.615(4) Å c = 29.674(6) Å	$\alpha = 90^\circ$. $\beta = 97.829(4)^\circ$. $\gamma = 90^\circ$.
Volume	7434(3) Å ³	
Z		4
Density (calculated)	1.667 Mg/m ³	
Absorption coefficient	2.465 mm ⁻¹	
F(000)		3828
Crystal size	0.20 x 0.18 x 0.10 mm ³	
Theta range for data collection	1.35 to 26.00°.	
Index ranges	-17 ≤ h ≤ 17, -21 ≤ k ≤ 21, -36 ≤ l ≤ 36	
Reflections collected	56771	
Independent reflections	14534 [R(int) = 0.1314]	
Completeness to theta = 26.00°	99.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.862 and 0.687	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14534 / 0 / 757	
Goodness-of-fit on F ²	0.925	
Final R indices [I > 2σ(I)]	R1 = 0.0798, wR2 = 0.1916	
R indices (all data)	R1 = 0.1516, wR2 = 0.2119	
Largest diff. peak and hole	1.585 and -1.812 e.Å ⁻³	

gd1

C84 H96 Br3 Gd O10 P4

1786.47

150(2) K

0.71073 Å

Monoclinic

P2(1)/c

 $a = 14.359(3) \text{ Å}$ $b = 17.682(4) \text{ Å}$ $c = 29.461(7) \text{ Å}$ $7408(3) \text{ Å}^3$

4

 1.602 Mg/m^3 2.662 mm^{-1}

3636

 $0.19 \times 0.18 \times 0.06 \text{ mm}^3$ $1.40 \text{ to } 25.00^\circ$ $-17 \leq h \leq 17, -20 \leq k \leq 21, -34 \leq l \leq 34$

52030

 $13017 [R(\text{int}) = 0.1260]$

99.9 %

Empirical

0.862 and 0.598

Full-matrix least-squares on F^2 $13017 / 0 / 757$

0.914

 $R1 = 0.0673, wR2 = 0.1475$ $R1 = 0.1343, wR2 = 0.1656$ $1.256 \text{ and } -1.371 \text{ e.Å}^{-3}$

yb1

C78 H78 Br3 O7 P4 Yb

1664.05

150(2) K

0.71073 Å

Triclinic

P-1

 $a = 14.662(3) \text{ Å}$ $b = 15.432(3) \text{ Å}$ $c = 17.610(4) \text{ Å}$ $3547.9(13) \text{ Å}^3$

2

 1.558 Mg/m^3 3.152 mm^{-1}

1674

 $0.40 \times 0.36 \times 0.28 \text{ mm}^3$ $1.30 \text{ to } 26.00^\circ$ $-18 \leq h \leq 18, -18 \leq k \leq 19, -21 \leq l \leq 21$

27672

 $13755 [R(\text{int}) = 0.0335]$

98.7 %

Empirical

0.862 and 0.576

Full-matrix least-squares on F^2 $13755 / 0 / 757$

0.933

 $R1 = 0.0310, wR2 = 0.0692$ $R1 = 0.0404, wR2 = 0.0708$ $1.642 \text{ and } -1.093 \text{ e.Å}^{-3}$

Table 2 Selected bond distances and angles

	Nd	Gd	Yb
Distances/Å			
Ln(1)-Br(1)	2.8617(13)	2.8099(12)	2.7650(6)
Ln(1)-Br(2)	2.8530(13)	2.8088(13)	2.7496(6)
Ln(1)-O(1)	2.305(7)	2.270(6)	2.172(2)
Ln(1)-O(2)	2.294(7)	2.272(6)	2.213(2)
Ln(1)-O(3)	2.334(6)	2.269(6)	2.197(2)
Ln(1)-O(4)	2.329(6)	2.253(6)	2.174(2)
P(1)-O(1)	1.516(7)	1.500(6)	1.510(2)
P(2)-O(2)	1.525(7)	1.500(6)	1.507(2)
P(3)-O(3)	1.479(7)	1.503(6)	1.501(2)
P(4)-O(4)	1.502(7)	1.516(6)	1.506(2)
Angles/°			
Br(1)-Ln(1)-Br(2)	176.15(4)	176.92(4)	179.021(13)
O(1)-Ln(1)-Br(1)	95.93(18)	86.92(15)	87.26(6)
O(1)-Ln(1)-Br(2)	87.19(18)	90.63(15)	91.81(6)
O(1)-Ln(1)-O(2)	90.5(2)	92.2(2)	89.80(8)
O(1)-Ln(1)-O(3)	173.0(2)	173.9(2)	174.45(8)
O(1)-Ln(1)-O(4)	87.2(2)	89.8(2)	88.94(9)
O(2)-Ln(1)-Br(1)	90.38(16)	90.24(14)	92.46(6)
O(2)-Ln(1)-Br(2)	91.85(16)	87.98(15)	87.83(6)
O(2)-Ln(1)-O(3)	89.8(2)	88.5(2)	89.48(8)
O(2)-Ln(1)-O(4)	176.7(2)	177.0(2)	173.41(8)
O(3)-Ln(1)-Br(1)	91.08(16)	87.07(15)	87.28(6)
O(3)-Ln(1)-Br(2)	85.79(16)	95.40(15)	93.66(6)
O(3)-Ln(1)-O(4)	92.7(2)	89.7(2)	92.38(9)
O(4)-Ln(1)-Br(1)	87.49(16)	92.05(15)	93.94(6)
O(4)-Ln(1)-Br(2)	90.42(16)	89.81(15)	85.74(6)
P(1)-O(1)-Nd(1)	167.3(4)	170.5(4)	158.39(14)
P(2)-O(2)-Nd(1)	173.6(4)	173.2(4)	155.52(14)
P(3)-O(3)-Nd(1)	172.8(4)	167.4(4)	166.43(14)
P(4)-O(4)-Nd(1)	173.0(4)	174.7(4)	163.18(14)

Table 3 Conductance data^a for LnBr₃(Ph₃PO)₄ in methanol and dichloromethane

$\Lambda_m / \text{Sm}^2\text{mol}^{-1}$ at 20°C		
Ln	Solvent	
	CH ₃ OH	CH ₂ Cl ₂
Ce	0.0140	0.0027
Pr	0.0152	0.0027
Nd	0.0152	0.0032
Gd	0.0156	0.0043
Tb	0.0156	0.0046
Dy	0.0163	0.0049
Er	0.0164	0.0050
Yb	0.0161	0.0052
Lu	0.0164	0.0055

a. Freshly prepared 0.001M solutions.

Table 4 ^{31}P NMR data at 20°C for $\text{LnBr}_3(\text{Ph}_3\text{PO})_4$ in CD_2Cl_2 and CD_3OD

	CD_2Cl_2		CD_3OD	
	δ / ppm (%) ^a	$\Delta\nu_{1/2}$ / Hz ^b	δ / ppm (%) ^a	$\Delta\nu_{1/2}$ / Hz ^b
Pr	158.7 (100)	254	38.4 (100)	116
Tb	-32.9 (90) -75.6 (10)	210	32.5 (100)	236
Er	-98.2 (15) -117.2 (85)	210	31.8 (100)	260
Lu	39.2 (95) 38.8 (5)	8	40.2 (25) 34.4(75)	73 132

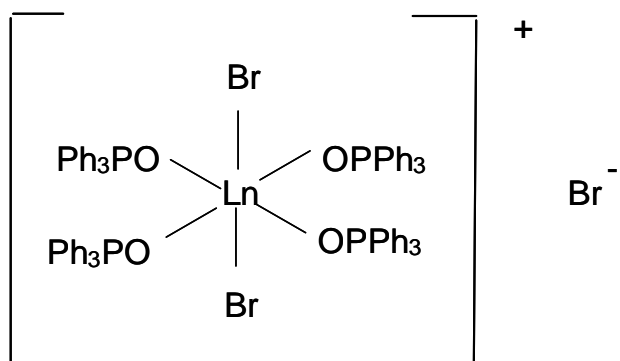
a. Percentage based on integrated NMR signals.

b. Line width at half height.

Table 5 Principle ions observed in the positive ion electrospray mass spectra of $\text{LnBr}_3(\text{Ph}_3\text{PO})_4$ ¹ in methanol

	Ce	Pr ²	Nd	Gd ²	Tb ²	Dy ²	Er ²	Yb ³
$\text{LnBr}_2\text{L}_4^+$	1412.0836	1413.0863	1416.087	1430.1024	1431.1072	1436.1092	1440.111	1446.1191
	30	65	100	75	25	15	55	40
$\text{LnBr}_2\text{L}_3^+$				1152.0168	1153.0202	1158.0229	1162.025	1168.0328
				10	5	<5	5	5
LnBrL_5^{2+}	805.6266	806.1281	807.6288	813.6357	815.1391	816.6398	819.1405	821.6445
	25	15	30	25	10	5	25	20
LnBrL_4^{2+}	666.5828	667.0841	668.5853	674.5920	676.0950	677.5960	679.5962	682.6008
	25	50	40	45	25	20	40	15
LnBrL_3^{2+}	527.5391	528.0405	529.5421	535.5486	536.0516	538.0517	540.5527	543.5570
	15	45	35	40	20	25	40	15
LnL_6^{3+}	603.1407	603.4752	604.1416	608.8135	609.4827	610.8165	612.1498	614.1528
	100	20	30	45	15	10	50	10
LnL_5^{3+}	510.4446	517.0888	511.4459	516.1175			519.4535	521.4568
	25	55	10	25			60	15
LnL_4^{3+}	417.4158	417.7500	418.4173	423.4225	423.7571	425.4252	426.7588	428.7615
	20	5	<5	10	5	<5	15	<5

1. L = Ph_3PO
2. Base peak at $m/z = 279.0936$ assigned as $[\text{Ph}_3\text{POH}]^+$
3. Base peak at $m/z = 857.2485$ assigned as $[\text{Ph}_3\text{PO}]_3\text{Na}^+$



Graphical Abstract (pictogram)

* Graphical abstract (synopsis)

The complexes $[\text{LnBr}_2(\text{Ph}_3\text{PO})_4]^+\text{Br}^-$ were prepared by the reaction of hydrated lanthanide bromides with triphenylphosphine oxide in ethanol. The structures of the Nd, Gd and Yb complexes are *trans* octahedral. The ^{31}P NMR spectra indicate the presence of more than one complex in solution for the heavier lanthanides.